EV237677546US

Patent-Treuhand-Gesellschaft
für elektrische Glühlampen mbH., Munich

Phosphor for light sources and associated light source

Technical field

The invention is based on a phosphor for light sources and an associated light source in accordance with the preamble of claim 1. It relates in particular to a yellow-emitting garnet phosphor for excitation by a light source with short wavelengths in the visible blue spectral region, with the result that white light is generated. A lamp (primarily a fluorescent lamp) or an LED (light-emitting diode) is particularly suitable as the light source.

Prior art

WO 98/05078 has already disclosed a phosphor for light sources and an associated light source. In that document, the phosphor used is a garnet of the structure $A_3B_5O_{12}$, the host lattice of which, as first component A, comprises at least one of the rare earths Y, Lu, Sc, La, Gd or Sm. Furthermore, one of the elements Al, Ga or In is used for the second component B. The only dopant used is Ce.

A very similar phosphor is known from WO 97/50132. The dopant used in that document is either Ce or Tb. While Ce emits in the yellow spectral region, the emission from Tb is in the green spectral region. In both cases, the complementary color principle (blue-emitting light source and yellow-emitting phosphor) is used to achieve a white luminous color.

Finally, EP-A 124 175 describes a fluorescent lamp which, in addition to a mercury fill, contains a plurality of phosphors. These are excited by UV

radiation (254 nm) or also by short-wave radiation at 460 nm. Three phosphors are selected in such a way that they add up to form white (color mixture).

Explanation of the invention

It is an object of the present invention to provide a phosphor in accordance with the preamble of claim 1 which is able to withstand high thermal loads and is eminently suitable for excitation in the short-wave visible spectral region.

This object is achieved through the characterizing features of claim 1. Particularly advantageous configurations are given in the dependent claims.

According to the invention, for light sources from which the emission lies in the short-wave optical spectral region, a phosphor which has a garnet structure $A_3B_5O_{12}$ and which is doped with Ce is used, the second component B representing at least one of the elements Al and Ga and the first component A containing terbium. Surprisingly, it has been found that under particular circumstances, namely under blue excitation in the range from 420 to 490 nm, terbium (Tb) is suitable as a constituent of the host lattice (first component of the garnet) for a yellow-emitting phosphor, the activator of which is cerium. Previously, in this context Tb has only been considered as an activator or coactivator, together with cerium, for emission in the green region, if excitation is produced by cathode rays (electrons) or short-wave UV photons (GB-A 1 600 492 and EP-A 208 713).

In this case, terbium, as the principal constituent of the first component A of the garnet, can be used on its own or together with at least one of the rare earths Y, Gd, La and/or Lu.

At least one of the elements Al or Ga is used as the second component. The second component B may additionally contain In. The activator is cerium. In a particularly preferred embodiment, a garnet of the structure

$(Tb_{1-x-y}RE_xCe_y)_3(Al,Ga)_5O_{12}$, where

RE = Y, Gd, La and/or Lu;

$0 \le x \le 0.5-y$;

$0<y<0.1$ is used.

The phosphor absorbs in the range from 420 to 490 nm and can thus be excited by the radiation from a blue light source, which is in particular the radiation source for a lamp or LED. Good results have been achieved with a blue LED whose emission peak was at 430 to 470 nm. The emission peak of the Tb-garnet: Ce phosphor is at approximately 550 nm.

This phosphor is particularly useful for use in a white LED based on the combination of a blue LED with the Tb-garnet-containing phosphor, which is excited by absorption of part of the emission from the blue LED and the emission from which supplements a remaining radiation from the LED, to form white light.

A Ga(In)N-LED is particularly suitable as the blue LED, but any other route for producing a blue LED which emits in the range from 420 to 490 nm is also suitable. 430 to 470 nm is particularly recommended as the principal emission region, since this is where efficiency is highest.

By selecting the type and quantity of rare earths, it is possible to fine-tune the location of the absorption and emission bands, in a similar way to that which is

known from the literature for other phosphors of type YAG:Ce. In conjunction with light-emitting diodes, it is particularly suitable for x to be $0.25 \le x \le 0.5 - y$.

The particularly preferred range for y is $0.02 < y < 0.06$.

The phosphor according to the invention is also suitable for combination with other phosphors.

A garnet of structure
$(Tb_xRE_{1-x-y}Ce_y)_3(Al,Ga)_5O_{12}$,

where RE = Y, Gd, La and/or Lu;
$0 \le x \le 0.02$, in particular $x = 0.01$;
$0 < y < 0.1$ has proven particularly suitable as the phosphor. Y frequently lies in the range from 0.01 to 0.05.

Generally, relatively small amounts of Tb in the host lattice serve primarily to improve the properties of known cerium-activated phosphors, while the addition of relatively large amounts of Tb can be used in a controlled way in particular to shift the wavelength of the emission from known cerium-activated phosphors. Therefore, a high proportion of Tb is particularly suitable for white LEDs with a low color temperature of below 5000 K.

Figures

The invention is to be explained in more detail below with reference to a number of exemplary embodiments. In the drawing:

Figure 1 shows an emission spectrum of a first Tb-garnet phosphor;

Figure 2 shows the reflectance spectrum of this Tb-garnet phosphor;

Figure 3 shows emission spectra of further Tb-garnet phosphors;

Figure 4 shows reflectance spectra of the Tb-garnet phosphors from Figure 3;

Figure 5 shows emission spectra for further Tb-garnet phosphors;

Figure 6 shows reflectance spectra for the Tb-garnet phosphors from Figure 5;

Figure 7 shows an emission spectrum for a white LED with Tb-garnet phosphor.

Description of a number of exemplary embodiments

Exemplary Embodiment No. 1:

The components

9.82 g	Yttrium oxide Y_2O_3
2.07 g	Cerium oxide CeO_2
37.57 g	Terbium oxide Tb_4O_7
26.41 g	Aluminum oxide Al_2O_3
0.15 g	Barium fluoride BaF_2
0.077 g	Boric acid H_3BO_3

are mixed and comminuted together for two hours in a 250 ml polyethylene wide-necked bottle using 150 g of aluminum oxide balls with a diameter of 10 mm. Barium fluoride and boric acid serve as fluxes. The mixture is annealed for three hours in a covered corundum crucible at 1550°C in forming gas (nitrogen containing 2.3% by volume hydrogen). The annealed material is milled in an automatic mortar mill and screened through a screen with a mesh width of 53 μm. This is followed by a second anneal for three hours at 1500°C under forming gas (nitrogen containing 0.5% by volume hydrogen). Then, milling and screening is carried out as after the first anneal. The phosphor obtained corresponds to the composition $(Y_{0.29}Tb_{0.67}Ce_{0.04})_3Al_5O_{12}$. It has a strong yellow body color. An emission spectrum for this

phosphor when excited at 430 nm and a reflectance spectrum for the phosphor between 300 and 800 nm are shown in Figures 1 and 2.

Exemplary Embodiment No. 2:

The components

43.07 g	Terbium oxide Tb_4O_7
1.65 g	Cerium oxide CeO_2
21.13 g	Aluminum oxide Al_2O_3
0.12 g	Barium fluoride BaF_2
0.062 g	Boric acid H_3BO_3

are intimately mixed as described under Example No. 1. Two anneals and the further processing of the annealed products take place as described under Example 1. The phosphor obtained corresponds to the overall composition $(Tb_{0.96}Ce_{0.04})_3Al_5O_{12}$ or, in the representation which illustrates the host lattice, $Tb_3Al_5O_{12}$:Ce. It has a strong yellow body color. The X-ray diffraction diagram shows that there is a cubic garnet phase. The emission spectrum and reflectance spectrum for this phosphor are shown in Figures 3 and 4, respectively.

Exemplary Embodiment No. 3:

The components

32.18 g	Yttrium oxide Y_2O_3
0.56 g	Terbium oxide Tb_4O_7
2.07 g	Cerium oxide CeO_2
26.41 g	Aluminum oxide Al_2O_3
0.077 g	Boric acid H_3BO_3

are intimately mixed as described under Example No. 1. Two anneals and processing of the annealed products take place as described under Example No. 1. The phosphor obtained corresponds to the composition

$(Y_{0.95}Tb_{0.01}Ce_{0.04})_3Al_5O_{12}$. It has a strong yellow body color. The emission spectrum and reflectance spectrum for this phosphor are shown in Figures 3 and 4, respectively.

<u>Exemplary Embodiment No. 4:</u>

The components

26.76 g	Yttrium oxide Y_2O_3
9.53 g	Terbium oxide Tb_4O_7
2.07 g	Cerium oxide CeO_2
26.41 g	Aluminum oxide Al_2O_3
0.149 g	Barium fluoride BaF_2
0.077 g	Boric acid H_3BO_3

are intimately mixed as described under Example No. 1. Two anneals and processing of the annealed products take place as described under Example No. 1. The phosphor obtained corresponds to the composition $(Y_{0.79}Tb_{0.17}Ce_{0.04})_3Al_5O_{12}$. It has a strong yellow body color. The emission spectrum and reflectance spectrum for this phosphor are shown in Figures 3 and 4, respectively.

<u>Exemplary Embodiment No. 5</u>

The components

30.82 g	Yttrium oxide Y_2O_3
0.56 g	Terbium oxide Tb_4O_7
4.13 g	Cerium oxide CeO_2
26.41 g	Aluminum oxide Al_2O_3
0.149 g	Barium fluoride BaF_2
0.077 g	Boric acid H_3BO_3

are intimately mixed as described under Example No. 1. Two anneals and processing of the annealed products are carried out as described under Example No. 1. The

phosphor obtained corresponds to the composition $(Y_{0.91}Tb_{0.01}Ce_{0.08})_3Al_5O_{12}$. It has a strong yellow body color.

Exemplary Embodiment No. 6:

The components

43.07 g	Terbium oxide Tb_4O_7
1.65 g	Cerium oxide CeO_2
21.13 g	Aluminum oxide Al_2O_3
0.062 g	Boric acid H_3BO_3

are intimately mixed as described under Example No. 1. Two anneals and processing of the annealed products are carried out as described under Example 1, except that the annealing temperature during the two anneals is lower by 50°C in each case. The phosphor obtained corresponds to the composition $(Tb_{0.96}Ce_{0.04})_3Al_5O_{12}$. It has a strong yellow body color. The emission spectrum and reflectance spectrum for this phosphor are shown in Figures 5 and 6, respectively.

Exemplary Embodiment No. 7:

The components

43.07 g	Terbium oxide Tb_4O_7
1.65 g	Cerium oxide CeO_2
17.05 g	Aluminum oxide Al_2O_3
7.50 g	Gallium oxide Ga_2O_3
0.062 g	Boric acid H_3BO_3

are intimately mixed as described under Example No. 1. Two anneals and processing of the annealed products are carried out as described under Example 1, except that the annealing temperature for the two anneals is lower by 50°C in each case. The phosphor obtained corresponds to the composition $(Tb_{0.96}Ce_{0.04})Al_4GaO_{12}$. It has a strong

yellow body color. The emission spectrum and reflectance spectrum for this phosphor are shown in Figures 5 and 6, respectively.

Exemplary Embodiment No. 8:

The components

43.07 g	Terbium oxide Tb_4O_7
1.65 g	Cerium oxide CeO_2
12.97 g	Aluminum oxide Al_2O_3
15.00 g	Gallium oxide Ga_2O_3
0.062 g	Boric acid H_3BO_3

are intimately mixed as described under Example No. 1. Two anneals and processing of the annealed products are carried out as described under Example 1, except that the annealing temperature for the two anneals is lower by 50°C in each case. The phosphor obtained corresponds to the composition $(Tb_{0.96}Ce_{0.04})_3Al_3Ga_2O_{12}$. It has a yellow body color. The emission spectrum and reflectance spectrum of this phosphor are shown in Figures 5 and 6, respectively.

Exemplary Embodiment No. 9

The components

4.88 kg	Yttrium oxide Y_2O_3
7.05 kg	Gadolinium oxide Gd_2O_3
161.6 g	Terbium oxide Tb_4O_7
595 g	Cerium oxide CeO_2
7.34 kg	Aluminum oxide Al_2O_3
5.50 g	Boric acid H_3BO_3

are mixed for 24 hours in a 60 l polyethylene vessel. The mixture is introduced into annealing crucibles made from aluminum oxide with a capacity of approx. 1 l and is annealed in a pushed-bat kiln for 6 hours at 1550°C

under forming gas. The annealed material is milled in an automatic mortar mill and then finely screened. The phosphor obtained has the composition $(Y_{0.50}Gd_{0.45}Tb_{0.01}Ce_{0.04})_3Al_5O_{12}$. It has a strong yellow body color. The emission spectrum and reflectance spectrum for this phosphor are shown in Figures 3 and 4, respectively.

Exemplary Embodiment 10 (LED):

When these phosphors are used in a white LED together with GaInN, a structure similar to that described in WO 97/50132 is employed. By way of example, identical fractions of phosphor in accordance with Example 1 and of phosphor in accordance with Example 4 are dispersed in epoxy resin and a LED with an emission peak of approximately 450 nm (blue) is encapsulated by this resin mixture. The emission spectrum of a white LED obtained in this way is shown in Figure 7. In this case, the mixture of the blue LED radiation with the yellow phosphor emission results in a color locus of x = 0.359/y = 0.350, corresponding to white light of color temperature 4500 K.

The phosphors described above generally have a yellow body color. They emit in the yellow spectral region. When Ga is added or used on its own instead of Al, the emission shifts more toward green, so that it is also possible in particular to achieve higher color temperatures. In particular, Ga-containing (or Ga,Al-containing) Tb-garnets and purely Al-containing Tb-garnets can be used in mixed form in order to be able to adapt to desired color loci.